

## PURIFYING APPARATUS

## BACKGROUND OF THE INVENTION

## 1. Field of the Invention:

The present invention relates to a purifying apparatus for flowing water. More detailedly, the invention relates to a purifying apparatus by oxidation and decomposition of water pollution substances in a river, which is effective for use such as elimination of nitrogen and phosphorous which are cause substances of eutrophication of the river flowing water.

## 2. Description of the Related Art:

Hitherto, in regard to a purification of the water pollution substances in the river, although a contact oxidation method by a biological membrane having a membrane in which microbes living in the river naturally grow has been developed and applied, this method is suitable mainly to purify carbon sources contained in a waste water, but it is not suitable to eliminate nitrogen and phosphorous which are cause substances of eutrophication.

Therefore, in prior arts, in order to prevent the eutrophication it is necessary to decompose and eliminate nitrogen and phosphorous other than the carbon sources, so that the biological membrane treatment method is not necessarily sufficient. Further, there have been studied about countermeasures such as a nitrification/denitrification by a

nutrient salt inclusive fixing method in which the biological membrane has been more strengthened and about an application of an ammonia phosphate crystallizing method using Mg salt, but they have such serious shortcomings that an elimination rate of nitrogen cannot exceed 60% in case where the ammonia in the river is eliminated, that a sufficient elimination rate cannot be ensured depending on a C/N ratio, and that even if a dissolved oxygen is sufficiently ensured in the river flow the nitrification does not proceed because a reaction velocity of nitrifying bacteria is low for the nitrification of ammonia form nitrogen. Accordingly, means for increasing the elimination rate of nitrogen and phosphorous to 90% or higher has become necessary at any cost.

#### SUMMARY OF THE INVENTION

Therefore, an object of the invention is to provide a new purifying apparatus capable of effectively eliminating the water pollution substances such as nitrogen and phosphorous in the flowing water in the river and the like, thereby solving the problems mentioned above of the prior art.

As one for achieving the above object the invention provides a purifying apparatus for flowing water in which a negative electrode plate is disposed on a flowing water bed and a positive electrode plate is disposed in an upper face oppositely to the negative electrode plate, characterized in

that the positive electrode plate is adapted so as to be dipped below a water surface of the flowing water with floats being disposed at least any of front/back and left/right of the positive electrode plate in a flowing direction of the flowing water, in the positive electrode plate there is arranged means for disposing it to an opposed upper face position with respect to the negative electrode plate, and the positive electrode plate and the negative electrode plate are provided with an electric field generating means, so that water pollution substances contained in the flowing water are oxidized and decomposed by a generation of high electric field pulses.

The invention intends to solve the problems by means of generating O-radical (oxygen radical) and OH-radical (hydroxy radical), which are generated by the high electric field pulses and have a high oxidizing power, on a metal face for nanosecond to microsecond, oxidizing mainly a carbon source and a nitrogen source in a polluted water, which impinge against these radicals, and cohering phosphorous by a cohesive reaction of particles in accompaniment with an electrification of  $H^+$  ions generated on this occasion to floating suspended substances so as to sediment and separate the phosphorous, thereby achieving by one pass operation an elimination of the pollution substances at 90 - 95% which could not be attained by the prior art.

And, in a concrete implementation mode, since a water

level and a flow rate of the flowing water change together with a structure of the purifying apparatus, in order to cope with this, the fact is taken into consideration that it is necessary to automatically control a supplied watt-hour by the flow rate of the water and a concentration of SS such that it becomes a suitable optimum watt-hour to thereby maintain the elimination rate of the pollution substances constant. For example, since the flowing water in water river greatly changes depending on time during one day and a ratio between when the flow rate is minimum and when it is maximum reaches 1 : 10 - 20, it follows that a magnitude of the flow rate is proportional to a passing velocity, so that, in order to supply an electric power tracing the magnitude of the flow rate, it is necessary to adjunctively provide a control unit for adjusting the supplied watt-hour which is optimum and minimum with respect to the flow rate, the floating suspended substances and a water depth. Further, in an emergency time such as a flood, the present apparatus must be provided for being shunted so as not to become an obstacle in the flowing water.

Therefore, first, in a structure of the purifying apparatus of the invention, the following modes are taken into consideration as being suitable ones, although not limited to these.

< 1 > In the positive electrode plate, there is provided means for vertically moving it.

< 2 > Gas collecting means (for collecting a gas generated by oxidation and decomposition) is provided.

< 3 > The positive electrode plate has at least one positive electrode substance among metals (including alloys; hereafter, ditto) and metal oxides.

< 4 > The positive electrode plate is composed, for example, of a base plate which is metal, ceramics or resin or a composite body of more than two of the formers, and of the positive electrode substance.

< 5 > The positive electrode substance is at least one of, for example, titanium oxide, ruthenium oxide, cobalt oxide, nickel oxide, tin oxide and platinum.

< 6 > In a more concrete example, in the positive electrode plate, at least one of titanium oxide, ruthenium oxide, cobalt oxide, nickel oxide, tin oxide and platinum is integrated with a plate of porous titanium, porous ceramics or stainless.

< 7 > The positive electrode plate is adapted such that its dipped depth from a water surface is  $1/5 - 1/10$  of a water depth.

In the invention adapted such that the water pollution substances contained in the flowing water are oxidized and decomposed by the generation of high electric field pulses, how the positive electrode plate should be constituted is practically a very important point in order to make the

generation of high electric field pulses and actions of the aforesaid radicals by the generation effective ones. More suitably, in the invention, as the positive electrode substance, the metal oxide or a noble metal is used. Such a metal oxide called titanium oxide, ruthenium oxide, cobalt oxide, nickel oxide or tin oxide, or platinum as mentioned above is effective.

As to the positive electrode substance, in case where it is the metal oxide, it may be one formed by making its particles into a green compact and baking or sintering it, or one in which the substance or its particles is/are born on a suitable base plate. As the base plate for bearing on this occasion, it may be, for example, a plate of porous titanium, porous ceramics or stainless etc., which has a high corrosion resistance, and it is preferable that the positive electrode substance constitutes a positive electrode face portion in a membrane-like form. The base plate itself may be made conductive, or the positive electrode substance in the membrane-like form may be caused to have a conductive property.

The metal oxide may be integrated with the base plate by an adhesion-integration by deposition, distillation and the like, or means such as application of a gel solution.

In case of platinum, a surface plating may be adopted, or a platinum foil may be adhered.

Incidentally, as to a negative electrode, various

substances may be adopted so long as they are metals having a high corrosion resistance or ones whose surfaces are coated with the metals. For example, a stainless plate and a metal plate coated with the platinum foil are exemplified.

It is practical that the positive electrode is adapted to be dipped from the water surface by vertically moving means and, further, it is desirable that the positive electrode plate is provided in its vicinity with gas collecting means.

Further, it is preferable in the invention that the positive electrode plate has a concave curved face opposite to the negative electrode in viewpoints of generating the high electric field pulses and collecting a decomposed gas.

Concretely exemplifying and explaining, for example, in the purification apparatus by oxidation and decomposition of the invention, the stainless plate or the metal plate coated with the platinum foil is made the negative electrode; titanium oxide, ruthenium oxide, cobalt oxide, nickel oxide, tin oxide or the platinum foil is adhered to an upper face of die-cast plate etc. of conductive porous titanium or stainless parallel in face to the metal plate; one in which the aforesaid upper face is slightly curved in a concave state relative to the negative electrode is made the positive electrode plate; floats are attached to the positive electrode plate at its front and back; there is provided a structure in which the positive electrode plate is dipped to  $1/5 - 1/10$  of a water depth; and

ther is provided a structure in which the floats are vertically movable at four corners of the positive electrode plate. Further, a sealing is applied in order to prevent a gas generated by the decomposition from escaping, and a gas reservoir is provided, thereby making it possible to collect the generated gas.

And, it is preferable that the purifying apparatus of the invention is adapted such that the water flow impinges against an oxidizing electrode face (positive electrode plate) under a turbulent flow state by high electrode field pulse waves, and an oxidizing reaction of pollution substances continues for at least 2 - 3 seconds. Further, as mentioned above, it is desirable to prevent the gas generated by oxidation and decomposition from being discharged into the air. Since the oxidizing reaction occurs by a physicochemical reaction,  $N_2$  and  $NO_x$  are generated in regard to N source, noxious gasses of  $SO_x$  and  $H_2S$  are generated in regard to S source, and  $CO_2$  gas is mostly generated and CO gas is slightly generated in regard to C source. It is desirable that these intermediate products are reduction-treated by hydrogen and the like. Treating means and treating unit therefor are also proposed in the invention.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig.1a is a side sectional view showing a constitution



of a purifying apparatus of the invention;

Fig.1b is a front sectional view showing the same;

Fig.2a is a side sectional view showing an example having an electric field control mechanism;

Fig.2b is a front sectional view showing the same;

Fig.3 is a side sectional view showing an example having a cleaner mechanism;

Fig.4 is a constitutional view showing an example having a gas catalyst oxidation unit; and

Fig.5 is a constitutional view showing an example having a sediment collecting unit.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Now, next, it is further explained about an implementation mode of the invention along the drawings. First. Fig.1a is a lateral sectional view showing main portions of a constitution of the purifying apparatus of the invention, and Fig.1b a front sectional view showing the same. A positive electrode plate is constituted as one in which a conductive porous metal (A) such as titanium for instance is made a base plate and to which there is integrally applied an oxide electrode or a platinum electrode (B), which consists of an oxide such as titanium oxide, ruthenium oxide, cobalt oxide, nickel oxide or tin oxide or platinum. Plural electrodes (B) are disposed orthogonally to a flowing direction ( $\alpha$ ) of the

⋮

•  
•  
•

•  
•  
•

THE UNIVERSITY OF CHICAGO PRESS  
530 N. Dearborn St., Chicago, Ill. 60610  
U.S.A. and Canada  
Outside N. America  
21, BEDFORD SQUARE, LONDON, W.1  
ENGLAND

such that a voltage between the positive electrode plate and the negative electrode plate is changed between 200 V/cm and 10 KV/cm. Further, a turbidimeter (Tu) as a concentration detector is provided in front of the flow, and an electric current is changed between 1 mA and 100 mA in compliance with the concentration. Further, a flow velocity meter (V) is arranged in a similar manner and, from the flow velocity, a frequency is changed between 10 kHz and 150 kHz. By such an automatic control mechanism, it follows that the oxidation and decomposition complying with a load amount of the water pollution is effectively performed. As to the automatic control mechanism, it is possible to further exemplify.

For example, like Fig.2a and Fig.2b, it is adapted such that positions of plus and minus are detected by the differential transformer (I), the flow rate is detected by the flow velocity meter (V), an SS amount is detected by the turbidimeter (Tu), a control unit (CPU) and an electric field generating unit (PA) are used, and these are made possible to perform controls of a voltage, a frequency, a pulse timing and a duty ratio by digital controls always as an optimum electric field treatment.

For example, in such examples of the invention as mentioned above, as shown also in Fig.1b and Fig.2b, the purifying apparatus is disposed within a width between side walls ( $\beta$ ) such as concrete. It is practically desirable to

dispose it in this manner.

And, in the oxidation/decomposition purifying apparatus of the invention, like Figs.1a, 1b and Figs.2a, 2b, as a suitable one there is shown one having a structure in which plural turbulent flow generating plates (G) each having a metal made protrusion are placed on the negative electrode plate (E) such that the water flow forms the turbulent flow with its height being limited to 10 - 15% of a distance between the electrode plates.

It is considered to make a backward angle of the protrusion about 20 - 40 degrees, and to dispose about 2 - 10 protrusions in the flowing direction of the water flow.

Further, in the river, since it is considered that suspended substances, sands and gravel enter into the apparatus, and in order to prevent an electrode face from deteriorating by the fact that the SS concentration is high, it is preferable, like Fig.3, to periodically perform a cleaning of the electrode face by a brush and a water jet by means of an automatic control. Further, at a flood time, since an outflow becomes larger than a planned water amount, it is effective to apply a provision for drawing up the plus electrode from an inside of the water, thereby immediately stopping loads of pulse waves.

Furthermore, in order to decompose a noxious gas such as NO<sub>x</sub>, SO<sub>x</sub> and H<sub>2</sub>S, like Fig.4, it is possible to reduce the

gas by means of a catalyst (d) by mixing the gas in a gas mixing unit (C) with hydrogen generated by an electrolysis of the water or hydrogen supplied from an H<sub>2</sub> bomb (B), thereby intending to prevent the noxious gas from generating.

As a countermeasure for the flood time, it is desirable that, when the electrode has floated above a set water level as shown in Figs.1a and 1b, the electrode is lifted above the water surface by an electric motor to thereby intend a safety of the apparatus.

And, further, the SS is sedimented by, for example, a high electromagnetic treatment, and the phosphorous and the SS in the polluted water can be eliminated in 80 - 90% by means of gravity-sedimenting them by providing in a downstream side a sedimentation tank through a bypass system by a pump or a direct system and returning a supernatant liquid to the original river (Fig.5).

Now, hereunder, the invention is more detailedly explained about embodiments.

#### < Embodiment 1 >

In a U-shape groove of 0.5 x 0.5 x 0.5 m, side grooves of 1 - 20 L/min in the flow rate of a domestic waste water of about 200 households were treated by the purifying apparatus of the invention exemplified in Figs.2a, 2b and Fig.4. Qualities of the original water and the treated water are as shown in Table 1.

Table 1

	Original water	Treated water
COD <sub>Cr</sub>	45-50	1-2
T-N	20-30	2-3
NH <sub>3</sub> -N	18-25	1-2
NO <sub>3</sub> -N	3-5	0.1-0.2
T-P	3-5	0.1-0.2
SS	40-45	5-10

unit:mg/l

Operating conditions are as shown in Table 2.

Table 2

Voltage	4kV - 10kV
Electric current	2 - 10mA
Frequency	50 - 75kHz
Water depth*	10cm
Electrode (plus)	Titanium oxide (porous titanium base plate)
Electrode (minus)	SUS (stainless plate)

\* : Dammed

Further, concentrations of the generated gasses are as shown in Table 3, and the gas after having been catalyst-treated by means of nickel and copper by a hydrogen addition was decreased in its noxious gasses, and their contents were in the order of traces.

Table 3

	Generated gas	After H <sub>2</sub> -treatment
CO <sub>2</sub>	50 - 60%	50 - 60%
O <sub>2</sub>	1 - 2%	100 - 300 ppm
CO	0.1 - 0.2	10 - 20 ppm
N <sub>2</sub>	50 - 60%	50 - 60%
NO <sub>x</sub>	300 ppm	10 ppm,
SO <sub>x</sub>	0.01 - 0.02%	3 - 5%

< Embodiment 2 >

A life waste water (sewage) in Tsukuba-City was treated. As the positive electrode plate, there was used one in which a TiO<sub>2</sub> particles sol was partially applied to a surface of porous ceramics having a porosity of 30% such that its thickness became 2 - 3 mm, the ceramics is sintered at 500 - 600°C after being dried, and the applied portion was made an electrode face.

The gas generated by the decomposition was caused to pass through the air and thereafter collected.

Results of the treatment during two months of November to December are shown in Table 4.

Table 4

Flow rate (m <sup>3</sup> /hr)		TOC (mg/L)	T•N (mg/L)	T•p (mg/L)	SS (mg/L)
0.60	Original water	13.2±5.0	10.3±3.8	1.0±0.5	30±8
	Treated water	3.0±1.0	1.5±0.5	0.04±0.01	2±1
1.23	Original water	12.5±5.0	10.1±3.5	1.2±0.6	32±8
	Treated water	2.5±1.0	1.8±0.8	0.08±0.02	3±1.5

Section: 50cm x 75cm    Water depth: 30cm    Normal pressure: 5kv, 10kHz,  
Duty ratio: 5%    Positive electrode: TiO<sub>2</sub>    Negative electrode: Ti (Thickness  
3mm)

Also in case where ruthenium oxide, cobalt oxide, nickel oxide and tin oxide were used in place of TiO<sub>2</sub>, approximately similar results were obtained.

As detailedly explained above, by the invention, the effective elimination of the water pollution substances such as nitrogen and phosphorous which have hitherto been difficult to be eliminated becomes possible, so that it is made possible to perform the purification of the flow such as river with a high efficiency.